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Imaging the spatial distribution of π* states in graphene using aberration-corrected and monochromated STEM-EELS: towards orbital mapping

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Electronic states are paramount to most physical and chemical properties of materials. For instance, electronic orbitals are responsible for chemical bonding between atoms of a crystal. Their experimental observation at defects and interfaces would help to understand material properties better and to develop nanostructures with novel functionalities. Nevertheless, the visualization of orbitals in real space at the atomic scale remains elusive, and is mostly attempted by surface microscopy tools, thus only with surface sensitivity. However, using electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) allows to probe electronic transitions from core levels to momentum- and site-projected empty states, *i.e.,* orbitals, in the bulk of a crystal. The pertinence and feasibility of orbital mapping using STEM-EELS has been demonstrated experimentally in bulk rutile previously [1].

Here, we focus on graphene, whose inherent two-dimensionality presents surfaces as structural discontinuities. Unfortunately, mapping electronic orbitals by core-loss EELS in top-view on pristine graphene would not give chemical bonding contrast as a result of atomic site symmetry [2]. In this work, we propose to determine the extent of the ð* ($1s \rightarrow 2p_z$) state distribution in pristine graphene layers in side-view, and explore the mapping of ð* orbitals by monochromated EELS in an aberration-corrected STEM. Subtle effects such as channeling of the electron beam make the interpretation of fine structure maps complex and must be evaluated with the help of simulations. We interpret the experimental signals on the basis of inelastic channelling calculations (ICCs).

We consider a specimen made of a hexagonal SiC substrate, a graphene buffer layer and five 'free standing' graphene layers, capped with Bi_2Se_3. SiC was annealed at ~950°C for 15 min in a Si flux to produce a (3x3) reconstructed surface, and the growth of graphene in ultrahigh vacuum was achieved by subsequent SiC substrate heating to 1100-1400°C [3]. Cross-sectional lamellae were made by focused ion beam (FIB) to achieve a thickness of ~25 nm. The STEM-EELS work was performed using a Nion UltraSTEM100 MC, equipped with a monochromator, a C_5 Nion probe corrector, a Gatan Enfinium spectrometer, and operated at 60 kV. ICCs were implemented using a home-made code [4], with core-level excitations described in the framework of density functional theory.

The absolute intensity of the ð* fine structures is higher on the atomic planes, and as a result ð* states appear, perhaps counter-intuitively, essentially localized on the graphene layers. However, when normalized to the ó* intensity, the ð* fine structures are more intense in between atomic planes (Figure 1). The ð*/ó* ratio map shows intensity maxima in between graphene layers, as highlighted by the anti-correlated ð*/ó* and HAADF intensity profiles (Figure 2(a-c)). All maps (ð*, ó*, ð*/ó*) are well reproduced by ICCs, as shown by the excellent overlap of experimental and calculated ð*/ó* intensity profiles. ICCs also enable an evaluation of the effect of thickness on the orbital contrast. The ð* map of an extremely (unrealistically) thin specimen (0.43 nm) displays lobes outside the C planes, and additional intensity is also expected on the C columns (Figure 2(d)). For larger and more realistic thicknesses up to 25.6 nm, the ð* intensity becomes progressively more important on the graphene planes than outside (Figure 2(e)), in agreement with experiments.

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This work highlights the successful mapping of ð* states at high resolution in 'free-standing' graphene multilayers. The projected thickness plays a significant role on the expected orbital contrast, as demonstrated by ICCs. These results suggest that significant improvement will be expected only for specimens less than few nm thick [5].

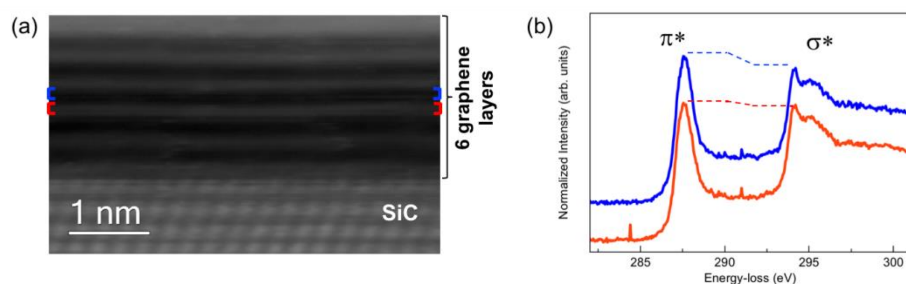

Figure 1. (a) High resolution STEM-HAADF image of a six-graphene layer assembly. (b) C-K edge spectra – shifted vertically for visualization – corresponding to on (red) and off (blue) the atomic planes, as indicated in (a).

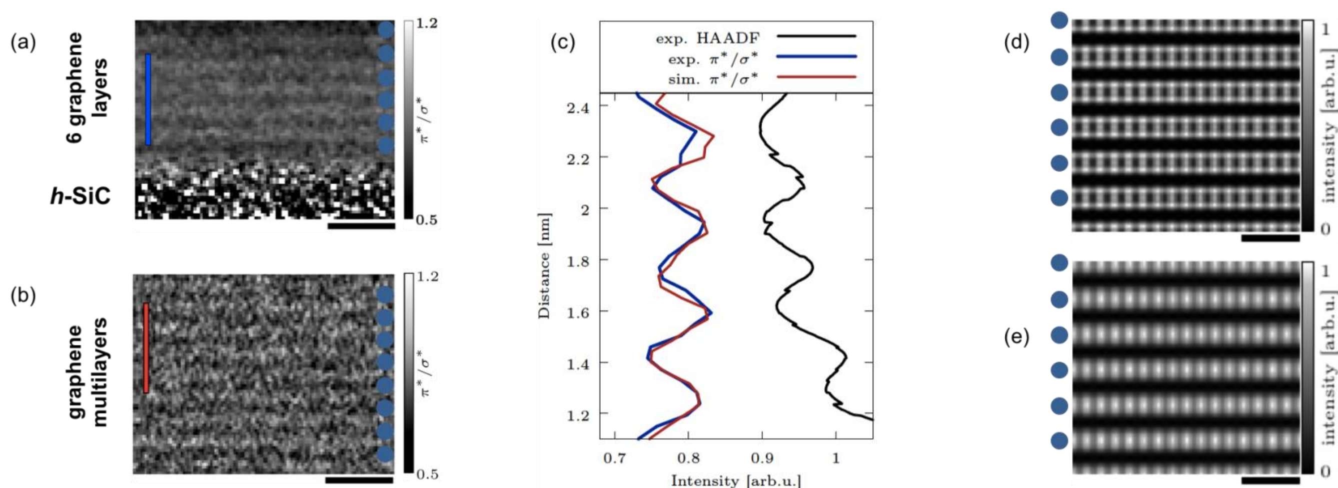

Figure 2. Experimental (a) and calculated (b) π*/σ* STEM-EELS maps. The position of the graphene layers is indicated by blue circles. (c) π*/σ* profiles from (a, b), and HAADF intensity integrated in the range indicated by the verticals blue (a) and red (b) bars. The calculated π*/σ* map in (b) was blurred with a Gaussian (1.1 Å standard deviation), and shot noise commensurate with that recorded in the experiments was added. Scale bars in (a, b) indicate 1 nm. (d) Calculated π* map of a specimen with 0.43 nm projected thickness, noise-free. (e) Calculated π* map (ICCs) of a specimen with 25.6 nm projected thickness, similar to the experimental value, noise-free. Scale bars in (d, e) indicate 0.5 nm.

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